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(54) **Developer sheet and imaging means, both for forming images.**

(57) Developer sheets for producing high density images, preferably in a photosensitive imaging system are disclosed. The developer sheet contains a particulate developer material which does not substantially compress upon the application of pressure to the sheet. The resistance to pressure is accomplished by using a developer sheet which has a discontinuous thickness or by incorporating a stilt material into the developer material. Also disclosed is imaging means which has a discontinuous thickness donor sheet to prevent the developer material from substantially compressing upon the application of pressure.

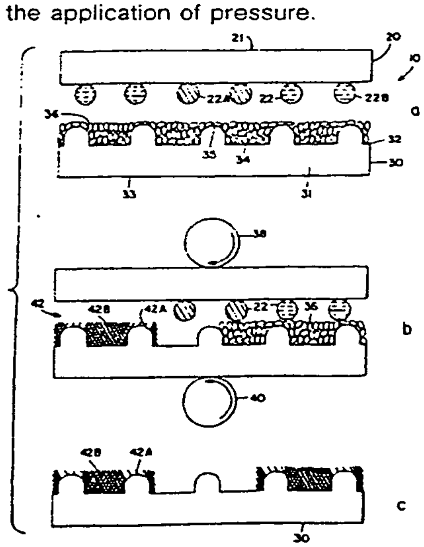

FIG. 1

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DEVELOPER SHEET AND IMAGING MEANS, BOTH FOR FORMING IMAGES

The present invention relates to the forming of images and more particularly to a developer sheet for forming high density images, and to imaging means.

Transfer carbonless copy systems and transfer imaging systems are well known in the art. These systems comprise two sheets which are used to form a visible image. The first sheet, the transfer or donor sheet, typically contains on one of its surfaces, a colourless colour-forming agent. Often, the colour-forming agent is contained in pressure rupturable microcapsules. The second sheet, the developer or receiver sheet, typically is a substrate having a layer of a developer material which reacts with the colourless colour-forming agent to form a visible image coated on to its front surface. In practice, to produce an image, the two sheets are aligned so that the colourless colour-forming agent faces the developer material. Upon the application of pressure, the colourless colour-forming agent reacts with the developer material on the developer sheet to form a visible image.

For a particular technical application, photosensitive imaging systems employing microencapsulated radiation sensitive compositions described in our U.S. Patent 4,399,209 and in our British Patent 2,113,860 have been developed. Imaging systems there described have an imaging sheet including a layer of microcapsules containing a photosensitive composition in the internal phase is image-wise exposed to actinic radiation. In the most typical embodiments, the photosensitive composition is a photopolymerizable composition including a polyethylenically unsaturated compound and a photoinitiator and is encapsulated with a colour former. The image-wise exposure hardens the internal phase of the microcapsules. Following exposure, the imaging sheet is assembled with a developer sheet and the assembly is subjected to a uniform rupturing force by passing the sheets through the nip between a pair of pressure rollers. Upon passing through the pressure rollers, the microcapsules image-wise rupture and release their internal phase whereupon the colour former migrates to the developer sheet and forms an image. The imaging system can be designed to produce monochromatic or polychromatic full colour images.

Although this system has proven to be quite successful, minor drawbacks still occur with respect to the developer sheet. More specifically, the developer material, which is typically a phenol formaldehyde novolak resin in particulate form, is susceptible to deformation as a result of the rupturing pressure. The deformation of the developer material on the receiver sheet is undesirable as this reduces the effective size of the pores between the particles of the developer material. According to a capillary model for oil transfer, the density of the image produced is proportional to the square root of the effective capillary radius of the developer material. In regions of high layer deformation, the effective capillary radius is smaller, and therefore, the density of the image is lower due to less efficient oil transfer in these areas.

In transfer systems, two types of materials are commonly used as developer sheets. The first material is a polymeric substrate, such as polyethylene terephthalate, coated with a developer material. The end product of such a receiver sheet is typically an overhead transparency. Because of the smooth and continuous surface of the polymeric substrate, when the developer material is coated onto the substrate, a uniform coating of particulate material is obtained. As such, when the developer sheet is assembled with the imaging sheet and subjected to pressure, the developer material uniformly deforms, thereby uniformly decreasing the pore size between developer particles. Accordingly, it has been particularly difficult to obtain high density images on clear polymeric substrates.

Alternatively, the other material traditionally used as a receiver sheet is paper. Depending on the paper selected, the texture of the surface of the paper containing the developer material often is discontinuous. For most photographic uses, the surface which contains the developer material has been pre-coated with a polymer coating to simulate the properties of the polymeric developer sheet. When the developer material is coated onto the polymeric coating, there are regions where the developer material is located at a greater paper thickness than in other regions. When the developer sheet is passed through pressure rollers, it has been discovered that the particles in the higher paper thickness regions are more likely to deform. Accordingly, in the lower paper thickness regions, a higher image density is achieved. Thus, the use of paper as a receiver material to some extent can produce a higher density image, and certainly a higher density image than that produced when using a polymeric receiver sheet. However, due to the substantial deviations in thickness of the paper, the images on the paper having high density versus the images having a low density are much more pronounced. Accordingly, the produced images can have a mottled appearance. This too is undesirable for obvious reasons.

A requirement of the above described transfer system is that a sufficient pressure must be exerted on the microcapsules to enable them to rupture and release their contents. As a result of the high rupturing pressure, it is inevitable that some developer material deformation will occur. One could hypothesize that to

improve the density of the produced image the rupturing pressure should be lowered. This does not necessarily result. If too low a pressure is used, not all of the image-forming microcapsules will rupture, and as a result, the desired high density images will not be obtained. In addition, not every point of the donor or imaging sheet contacts every point of the developer sheet. As a result, high pressures must be maintained across the donor or imaging sheet and developer sheet to insure a uniform contact. Accordingly, other means must be provided for remedying the pressure deformation defect of the developer sheet.

Thus, there exists a continuing need in the art for developer sheets which are capable of producing high density images and wherein the images produced are not mottled. The present invention has arisen from our work seeking to satisfy this need.

In accordance with the present invention, there is provided a developer sheet useful in forming images having a high density, said sheet comprising a support having front and back surfaces wherein said support is microroughened to provide a discontinuous texture; and a developer layer containing a particulate reactive material on said front surface, said reactive material being capable of reacting with a substantially colourless chromogenic material upon contact and generating an image.

In a second and alternative aspect thereof, the invention provides a developer sheet useful in forming images having a high density, said sheet comprising a support having front and back surfaces and a developer layer consisting essentially of a particulate reactive material and a stilt material on said front surface, said reactive material being capable of reacting with a substantially colourless chromogenic material upon contact and generating an image, and said stilt material being capable of absorbing a high pressure load to prevent said reactive material from substantially deforming upon the application of a high pressure load.

The invention provides, in a third alternative aspect thereof, a developer sheet useful in forming images having a high density, said sheet comprising: a support having front and back surfaces; a backing layer having front and back surfaces; and a developer layer containing a particulate reactive material; said front surface of said backing layer being attached to said back surface of said support, said backing layer being texturally discontinuous, said developer layer being located on said front surface of said support, and said reactive material being capable of reacting with a substantially colourless chromogenic material upon contact and generating an image.

Our sheets and imaging means as described in detail herein below, are designed so that when they are passed through pressure rolls, the developer material on the sheet is not substantially deformed because of the maintainance of a pressure differential across the developer material.

By maintaining a pressure differential across the developer sheet, the particulate developer material coated onto the sheet does not uniformly deform. Rather, the particles maintained in the areas of the sheet which are subjected to the greatest amount of pressure are more deformed than the areas which receive a lesser amount of pressure. In the areas of greater deformity, the image density will be slightly lower. By comparison, in the areas of less deformity, due to the increased pore size between developer particles, the images produced will have a higher density. By maximizing the number of high density image areas on the sheet, and maximizing the pore size between developer particles, the overall image produced will have a higher density.

It is a further concern of ours that the pressure differential across the developer sheet not be too great. If the variations between high image density areas and low image density areas are too great, as discussed above, the overall produced images may have a mottled appearance.

Accordingly, while our system as herein described may produce a small amount of mottle as a result of the low and high density areas, it is particularly preferred that the amount of mottle be maintained at a minimum.

Several alternatives may be utilized as developer sheets. For example, in one arrangement, the developer sheet comprises a support having front and back surfaces, and the front surface of said support is microroughened to produce a discontinuous textural surfaces, a particulate developer layer containing a reactive material is provided on said front surface, the reactive material being capable of reacting with a substantially colourless chromogenic material upon contact and generating an image.

By utilizing a developer sheet having a microroughened surface, the developer sheet will be such that some areas of the sheet containing the developer layer are thicker than others or less deformed than others. In the areas where the thickness of the sheet is greatest, when passed through pressure rolls, a higher pressure will be applied, and the developer material located at these areas will be susceptible to deformation. The high sheet thickness regions will bear most of the load as a result of the applied pressure. By comparison, in the areas where the developer material is located in between the higher thickness areas, less pressure will be applied. As such, the developer material in these areas will not significantly deform, and as a result, high density images are produced. By maintaining the number of high density areas at a

maximum, an overall high density image is produced. Further, as long as the substrate is designed so that the areas of high density and low density are closely spaced, and that the low density areas are small in size, the produced image will not suffer from a mottled appearance.

In another arrangement, the developer sheet comprises a support having front and back surfaces and has a developer layer containing a reactive particulate developer material on the front surface, the reactive material being capable of reacting with a substantially colourless chromogenic material upon contact and generating an image, and the developer layer further containing a stilt material to absorb a significant amount of the pressure applied by the pressure rollers.

The stilt material is particularly designed so that upon the application of high amounts of pressure, the material is relatively noncompressible, i.e. has a relatively high modulus of compression. As such, the developer particles located below the stilt particles do not significantly compress, and a significant pore volume is maintained between developer particles.

In still another arrangement, the developer sheet comprises a support having front and back surfaces, a backing layer having front and back surfaces, and a continuous developer layer containing a particulate reactive material. The front surface of the backing layer is attached to the back surface of the support . The backing layer is texturally discontinuous. The developer layer is on the front surface of the support, being capable of reacting with a substantially colorless chromogenic material upon contact and generating an image.

In this embodiment, it is the backing layer which enables the differential pressure load to be applied to the developer material. For example, in the areas where the backing layer is thickest, the highest pressure load will be exerted on the developer material whereas in the areas where the backing layer is not as thick, the pressure exerted on the developer material will be reduced. As discussed above, the maintenance of the differential pressure gradient across the particulate developer material enables the production of high density images.

In still another alternative aspect of the present invention, there is provided imaging means, comprising: a donor sheet comprising a support having front and back surfaces, a backing layer having front and back surfaces, and a receiver sheet having front and back surfaces; the donor sheet having a layer of microcapsules containing in their internal phases a substantially colourless chromogenic material coated on its front surface, the front surface of said backing layer being attached to the back surface of said donor sheet, and said backing layer being discontinuous in thickness; and said receiver sheet containing a developer material containing a particulate reactive material on its front surface, said reactive material being selected to be capable of reacting with said substantially colourless chromogenic material upon contact and to generate an image.

The backing layer located on the donor sheet acts to provide the pressure differential to prevent uniform deformation of the developer material. Only the areas of developer particles located directly below the highest thickness areas of the backing layer are susceptible to deformation.

We particularly envisioned that the developer sheet be a transparent polymeric material, or a polymer coated paper material. In embodiments wherein a coated paper material is selected, the coating is preferably treated to provide a pressure differential accross the coating.

We particularly envision that the developer sheet be used in an imaging system including an imaging sheet including a support having a layer of photosensitive microcapsules on the surface of the support. After image-wise exposure of the imaging sheet to actinic radiation, the imaging sheet and a developer sheet acting as receiver sheet are aligned and are passed through the nip of pressure rolls to rupture the microcapsules and enable the contents of the ruptured capsules to migrate to the developer material and produce a visible image.

The invention is hereinafter more particularly described by way of example only with reference to the accompanying drawings, in which:-

Figs. 1(a) - (c) schematically illustrate a developer sheet and imaging means and successive stages in their use in a first imaging system embodying the teachings of the instant invention;

Figs. 2(a) - (c) schematically illustrate a developer sheet and imaging means and successive stages in their use in an alternative imaging system embodying the teachings of the instant invention; and

Figs. 3(a) - (d) schematically illustrate a developer sheet and imaging means and successive stages in their use in another alternative imaging system also embodying the teachings of the instant invention.

The system described herein may be used for any transfer system containing a donor or imaging sheet and a developer sheet wherein the donor or imaging sheet contains an image-forming agent capable of reacting with a developer material to form an image, the developer sheet contains a developer material capable of reacting with the image-forming agent and wherein, to produce a visible image, the donor or imaging sheet is aligned with the developer sheet and pressure is applied to the sheets to cause transfer of

the image-forming agent to the developer sheet. It is particularly envisioned that our developer sheets be used in association with imaging sheets containing photosensitive microcapsules containing an image-forming agent. However, it is envisioned that the developer sheets may be adapted for use in association with any transfer image-forming system.

In a preferred embodiment, imaging means includes an imaging sheet having a layer of photosensitive microcapsules and a developer sheet. The imaging sheet, as well as the photosensitive compositions, photoinitiators, colour formers, wall formers, encapsulation techniques and developer materials described in our U.S. Patents Nos. 4,399,209; 4,772,530; and 4,772,541 are useful herein. The disclosures of these patents are to be regarded as effectively incorporated herein by reference.

Imaging means employing one embodiment of our developer sheet is shown in Fig. 1 and is represented by element 10. Imaging means 10 includes imaging sheet 20 and developer sheet 30. Imaging sheet 20 comprises a support 21 having a layer 22 of photosensitive microcapsules 22A and 22B coated on the surface thereof. The microcapsules, prior to exposure, typically contain as their internal phase a photohardenable composition and a colorless color-forming agent. The microcapsules shown in Fig. 1(a) have already been image-wise exposed to actinic radiation such that the internal phase of microcapsules 22A have photohardened whereas the internal phase of microcapsules 22B remain liquid. The exposure details and details of the internal phases of the microcapsules are more thoroughly described in U.S. Patent 4,399,209.

Developer sheet 30 includes substrate 31 having a front surface 32 and a back surface 33. Substrate 31 is made of transparent polymeric materials such as polyethylene terephthalate, translucent substrates, opaque polymeric substrates such as Melinex 329 and Melinex 470 sold by ICI Americas, or polymer coated paper materials. Coated paper materials include commercial available photographic papers. Front surface 32 is microroughened such that surface 32 has regions of higher substrate thickness 35 and regions of lower substrate thickness 34. The microroughening of surface 32 is obtained by calendaring the polymeric substrate or polymer coating against a roughened roller after formation of the substrate into a sheet, solvent etching the polymeric substrate or polymer coating after formation of the substrate into a sheet, including a pigment such as titania into the polymer material or coating prior to sheet formation or casting the polymeric material or coating against a rough surface prior to sheet formation.

Coated onto surface 32 is particulate developer material 36. As seen in Fig. 1(a), more developer material 36 is maintained on sheet 30 in the areas having regions of lower thickness 34 and less material 36 is maintained in the regions of higher thickness 35.

Referring to Fig. 1(b), the advantages of utilizing the microroughened substrate will be explained. To form an image on substrate 31, imaging sheet 20 and developer sheet 30 are aligned so that the walls of microcapsules 22 contact the layer of developer particles 36. They are then passed together, as an assembly, through pressure rolls 38 and 40. This causes the non-photohardened microcapsules 22B to rupture so that their internal phase contents release whereupon the image-forming agent contacts developer material 36 to form a visible image 42. In the areas laying directly above the higher substrate thickness areas 35, the image has a slightly lesser density because of developer particles 36 having been compressed as a result of the pressure created by rolls 38 and 40 and sheets 20 and 30 and is represented by element 42A. By comparison, the images produced in the areas laying directly above lower substrate thickness areas 34 have a higher density and are represented by element 42B. The high density images 42B result because the developer particles 36 located in these areas are not highly compressed, resulting in an increased pore volume for the chromogenic material to transfer to. Material 36 does not highly compress in these areas because most of the pressure which is exerted as a result of the forces of rollers 38 and 40 is absorbed by regions 35. Once sheets 20 and 30 have passed through rollers 38 and 40, sheet 20 is removed, leaving developer sheet 30 having high density images on its upper surface. The resultant sheet is shown in Fig. 1(c).

In the preferred embodiment, the distance between adjacent high substrate thickness areas 35 is approximately 10 to about 40 microns. This spacing enables the density of the overall image produced to be maintained at a maximum. In reality, as shown in Figs. 1(b) and 1(c), the produced image is actually an alternating pattern of high density and low density images. However, due to the intimate spacing, the overall appearance is one of a continuous, high density image. It is particularly important that the spacing between adjacent regions 35 not be too great as this will pronounce the high density-low density image effect and produce a mottled appearance.

An imaging system employing an alternative embodiment of developer sheet is shown in Fig. 2 and is represented by imaging means 100. Imaging means 100 includes imaging sheet 120 and developer sheet 130. Imaging sheet 120 is identical to sheet 20 of Fig. 1, and has already been image-wise exposed to actinic radiation.

Developer sheet 130 includes substrate 131 having a front surface 132 and a back surface 133 and is made of the same materials as described with respect to Fig. 1. Located on the front surface of 132 are pressure absorbing particles 134 and particulate developer material 136. Particles 134 are characterized by being noncompressible in that they do not substantially deform when subjected to pressure. These particles are typically known in the art of carbonless paper production as stilt materials and function primarily to prevent undesirable compression of developer particles 136.

Referring to Fig. 2(b), the advantages of utilizing the inventive substrate will be explained. As is the case with the system of Fig. 1, the imaging sheet 120 and developer sheet 130 are brought into alignment and are passed between pressure rollers 138 and 140. This causes the walls of microcapsules 122B to rupture and enable their internal phase to release and migrate to developer material 136 to form a visible image 142.

When pressure is exerted on developer sheet 130, particles 134, because of their noncompressible nature, act to absorb the pressure load. This provides protection to the developer material 136 located physically below the top of particles 134 on substrate 131. In the areas where developer material 136 is located above the top of particles 134, material 136 will be compressed as a result of the pressure forces. The produced images in these areas will not achieve a maximum color density and are indicated by 142A. However, in the areas where material 136 lies below the top of particles 134, particles 134 act to absorb the pressure forces and protect material 136 from undesirable compression. As a result, these areas are highly porous and high density images, as represented by element 142B, are produced.

As is the case with the system of Fig. 1, the resulting image, as shown in Fig. 2(c), has areas of high color density 142B and areas of low density 142A. However, because of the close spacing maintained between particles 134, typically between 10 microns and about 40 microns, the overall appearance is one of high color density. As is the case with the system of Fig. 1, the spacing of particles 134 must be intimate so that the high density image appears continuous and not mottled.

An imaging system employing another alternative embodiment of developer sheet is shown in Fig. 3 and is represented by imaging means 200. Imaging means 200 includes imaging sheet 220 and developer sheet 230. Imaging sheet 220 is identical to sheet 20 of Fig. 1, and has already been image-wise exposed to actinic radiation.

Developer sheet 230 includes substrate 231 having a front surface 232 and a back surface 233 and is made of the same materials as described with respect to Fig. 1. Located on front surface 232 is a uniform layer of particulate developer material 236. The thickness of layer 236 is about 10 microns. Attached to back surface 233 is releasable backing sheet 234. The face of sheet 234 attached to surface 233 is applied onto surface 233 by means known in the art, such as pressure sensitive adhesives. The use of a pressure sensitive adhesive enables sheet 234 to be easily released from substrate 231 after the development procedure has been completed.

Sheet 234 is discontinuous in thickness, having regions 235 of high sheet thickness and regions 237 of lower sheet thickness. The use of a release sheet having a discontinuous thickness enables the production of high color density images in a manner akin to that described above with respect to Fig. 1.

Referring to Fig. 3(b), sheets 220 and 230 are passed between pressure rollers 238 and 240 to cause the walls of microcapsules 222B to rupture. This causes the internal contents to release and contact developer material 236 to form a visible image 242. In the areas where pressure rollers 238 and 240 contact high sheet thickness regions 235, a greater amount of pressure is exerted upon sheets 220 and 230, causing developer material 236 located directly above these regions to slightly compress. As a result, the density of the produced image 242A is not as high as possible. By comparison, less pressure is exerted in the regions laying directly over lower sheet thickness regions 237. Thus, compression of these areas, and particularly developer material 236, is minimized, resulting in no substantial loss of porosity of the spaces between particles 236. The images produced in these areas 242B, are of a high density. Once imaging sheet 220 and developer sheet 230 have passed through rolls 238 and 240, backing sheet 234 is removed, leaving substrate 231 having located on its upper surface images of high density, 242B and of lower density 242A.

As is the cause with the system of Fig. 1, the space between adjacent high sheet thickness regions 235 is maintained between about 10 microns and about 40 microns to provide a visual image which appears to be of a uniform high density. If the space between adjacent high sheet thickness regions 235 is too great, a mottled appearance may occur.

In still another embodiment, not pictured, the developer sheet has a microroughened back surface. This embodiment is identical to that shown in Fig. 3 with the exception that the uneven thickness backing layer is not adhered to the developer substrate, but rather, is integrally formed onto the back surface of the developer sheet.

In still another embodiment, not pictured, the backing layer is attached to the donor sheet on the face not containing the microcapsules. As a result of the discontinuous thickness of the backing layer, a similar pressure profile to that discussed with respect to Fig. 3 is obtained to enable the production of high density images. In addition, because the imaging sheet is ultimately discarded, the backing layer need not be removed from the imaging sheet after transfer, or it may be integrally formed onto the imaging sheet.

The particulate reactive material in the developer layer of the developer sheet is selected such that it reacts with the chromogenic material associated with the microcapsules of the imaging sheet and produces a color image. In the most typical embodiments, the chromogenic material is a substantially colorless electron donating compound of the type conventionally used in the pressure-sensitive recording art and the developer material is an electron accepting compound.

The reactive developer can be selected from among the developers conventionally used in carbonless paper including acid clay, active clay, attapulgite, etc.; organic acids such as tannic acid, gallic acid, propylgallate; aromatic carboxylic acids such as benzoic acid, p-tert-butyl-benzoic acid, 4-methyl-3-nitrobenzoic acid, salicylic acid, 3-phenyl salicylic acid, 3-cyclohexyl salicylic acid, 3-tert-butyl-5-methyl salicylic acid, 3,5-di-tert-butyl salicylic acid, 3-methyl-5-benzyl salicylic acid, 3-phenyl-5-(α, α -dimethylbenzyl)salicylic acid, 3-cyclohexyl-5-α, α-dimethylbenzyl)salicylic acid, 3-(α,α -dimethylbenzyl)-5-methyl salicylic acid, 3,5-di-cyclohexyl salicylic acid, 3,5-di-(α-methylbenzyl)salicylic acid, 3,5-di-(α, α-dimethylbenzyl)-salicylic acid, 3-(α-methylbenzyl)-5-(α, α-dimethylbenzyl)salicylic acid, 4-methyl-5-cyclohexyl salicylic acid, 2-hydroxy-1-benzyl-3-naphthoic acid, 1-benzoyl-2-hydroxy-3-naphthoic acid, 3-hydroxy-5-cyclohexyl-2-naphthoic acid and the like, and polyvalent metallic salts thereof such as zinc salts, aluminum salts, magnesium salts, calcium salts and cobalt salts as disclosed in U.S. Patents 3,864,146; 3,924,027 and 3,983,292; phenol compounds such as 6,6′-methylenebis(4-chloro-m-cresol) as disclosed in Japanese Patent Publications 9,309 of 1965 and 20,144 of 1967, and Japanese Laid Open Patent Publication No. 14,409 of 1973; phenol resins such as phenol-aldehyde resins e.g., p-phenyl-phenol-formaldehyde resin and phenol-acetylene resins, e.g., p-tert-butylphenol-acetylene resin, and polyvalent metallic salts thereof such as zinc modified phenyl formaldehyde resin as disclosed in U.S. Patent 3,732,120; acid polymers such as maleic acid-rosin resin and copolymers of maleic anhydride with styrene, ethylene or vinylmethylether; and aromatic carboxylic acid-aldehyde polymers, aromatic carboxylic acid-acetylene polymers and their polyvalent metallic salts as disclosed in U.S. Patents 3,767,449 and 3,772,052.

The phenolic resins may be further modified to include amounts of unsubstituted or substituted salicylic acids in a manner known in the art.

Another class of phenolic resin useful in practice of the present invention is the product of oxidative coupling of substituted or unsubstituted phenols or bisphenols. Oxidative coupling may be catalyzed by various catalysts but a particularly desirable catalyst is the enzyme, horseradish peroxidase. Particularly desirable developers are the resins described in our U.S. Patent No. 4,647,952, the disclosure of which is to be regarded as hereby incorporated herein by reference, and more particularly the product of oxidative coupling of bisphenol A.

Especially preferred particulate developer materials are phenol-formaldehyde condensation products. More particularly, alkylphenolic resins and, still more particularly, metallated products of alkylphenolic resins are preferred. The alkyl phenols are monosubstituted by an alkyl group which may contain 1 to 12 carbon atoms. Examples of alkyl phenols are ortho- or para- substituted ethylphenol, propylphenol, butylphenol, amylphenol, hexylphenol, heptylphenol, octylphenol, nonylphenol, t-butylphenol, t-octylphenol, etc.

Another class of thermoplastic developer material which may be practiced within the scope of the present invention is a resin-like condensation product of a polyvalent metal salt, such as a zinc salt, and a phenol, a phenol-formaldehyde condensation product, or a phenol-salicylic acid-formaldehyde condensation product. This developer material is available from Schenectady Chemical Co. under the designation HRJ 4250 and HRJ 4542. These products are reported to be a metallated condensation product of an ortho- or para-substituted alkylphenol, a substituted salicylic acid, and formaldehyde.

Optionally incorporated with the thermoplastic developer material is one or more surfactants or plasticizers. The surfactant(s) or plasticizer(s) is selected to specifically complement the developer material to aid the developer material in coalescing and, particularly in the case of transparencies, to aid in coating. The material is preferably present in an amount of about .05 to 5 parts per 100 parts of developer material, more preferably about .5 to 1.5 parts per 100 parts. Examples of such materials include terphenyls and sodium sulfosuccinic acid.

The aforementioned developers are applied to the developer support in a conventional manner. They may be mixed with a binder latex, polyvinyl alcohol, maleic anhydride styrene copolymer, starch, gum arabic, etc., and coated on a substrate such as paper or coated directly. The thickness of the developer layer ranges from about 6 microns to about 15 microns.

When sheet 30, 130 or 230 is a transparent material or coating layer such as polyethylene terephthalate, developer material 36 may be overcoated with a discontinuous pigment (not pictured). As discussed in greater detail in U.S. Patent No. 4,554,235, after development, the receiver sheet may be heated or subjected to pressure to cause the pigment to fuse and form an essentially transparent glossy polymeric film over the developed image.

Typical examples of useful pigments are pigments obtained upon drying DOW XD 899301 latex, Dow 722 latex, Dow 788 latex, products of Dow Chemical Co., UCAR 4630x latex, UCAR 4510 latex, styrene-acrylic latices of Union Carbide Corp., polyvinyl acetate emulsion 202A, a product of Union Oil Company of California, polystyrene latices 5611 and 5612, products of Union Oil Co. of California, Polysar 1183, Polysar 9010-P and Polysar 1164, polystyrene latices of Polysar Latex Co., acrylic latex 200, a product of Union Oil Co. of California, polyvinylidene chloride lattices, 542 and MS-153, products of Union Oil Co. of California, Casco wax, a wax emulsion from Borden Co., and Paraco, a wax emulsion from Hercules Chemical Co. Because these latices are non-film forming, a small amount of a binder is usually used with the latex and adhere it to the developer sheet. Preferably, a binder is used in an amount of about 0.5 to 10% by weight based on the coated solid mixture. Suitable binders include starch, polyvinyl alcohol, gelatin, and film forming acrylic, vinyl acrylic and polyvinylidene chloride latices. The binder must not be used in an amount which creates a barrier to permeation of the layer by the internal phase.

The amount of the pigment applied to the developer layer is a function of the nature of the pigment and its particle size. Typically the pigment is employed at an application rate of about 0.1 to 10 g/m^2 and more preferably 0.5 to 5 g/m^2.

When the developer sheet such as that shown in Fig. 2 contains a stilt material as a pressure absorber, the stilt material should be selected from those materials known in the art. For example, stilt materials have been coated on imaging sheets to prevent color-forming microcapsules from inadvertently rupturing. See, for example, U.S. Patent Nos. 4,212,437; 4,268,069; 4,486,762; and 4,675,706. Examples of such stilt materials include cooked and uncooked starch particles, pulp and polyolefin materials. Hardened spherical particles such as photohardened microcapsules may also be utilized. In practice, the diameter of the stilt particles ranges from about 6 microns to about 20 microns to prevent undesirable compression of the developer material.

Positive-working photosensitive compositions useful in practice of the present invention usually include a photoinitiator in combination with a monomer, a dimer, or an oligomer which is polymerizable to a higher molecular weight compound, or a polymer which is crosslinked upon exposure. For a negative working material a compound which is depolymerizable or otherwise photolyzable upon exposure is used.

Ethylenically unsaturated organic compounds are useful photosensitive materials. These compounds contain at least one terminal ethylene group per molecule. Typically, liquid ethylenically unsaturated compounds having two or more terminal ethylene groups per molecule are preferred. Examples of this preferred subgroup are ethylenically unsaturated acid esters of polyhydric alcohols such as ethylene glycol dimethacrylate, triethylene glycol dimethacrylate, trimethylolpropane triacrylate (TMPTA) and trimethyol propane trimethacrylate. Another example of a useful radiation sensitive composition is an acrylate prepolymer derived from the partial reaction of pentaerythritol with acrylic acid, methacrylic acid, or acrylic or methacrylic acid esters. Another group of substances useful as photosensitive compositions include isocyanate modified acrylic, methacrylic and itaconic acid esters of polyhydric alcohols.

In most cases, the photosensitive composition includes a photoinitiator. It is possible to use either homolytic photoinitiators which are converted to an active species by radiation and generate a radical by abstracting a hydrogen from a hydrogen donor, or photoinitiators which complex with a sensitizer to produce a free radical generating species, or photoinitiators which otherwise generate radicals in the presence of a sensitizer. If the system relies upon ionic polymerization, the photoinitiator may be of the anion or cation generating type, depending on the nature of the polymerization.

Examples of photoinitiators useful in practice of the present invention include diaryl ketone derivatives, and benzoin alkyl ethers. The photoinitiator is selected based on the sensitivity of the system that is desired. Where ultraviolet sensitivity is desired, suitable photoinitiators include alkoxy phenyl ketones, O-acylated oximinoketones, polycyclic quinones, benzophenones and substituted benzophenones, xanthones, thioxanthones, halogenated compounds such as chlorosulfonyl and chloromethyl polynuclear aromatic compounds, chlorosulfonyl and chloromethyl heterocyclic compounds, chlorosulfonyl and chloromethyl benzophenones and fluorenones, and haloalkanes. In many cases it is advantageous to use a combination of imaging photoinitiators.

For use as visible light photoinitiators, the reactive dye-counter ion photoinitiators disclosed in U.S. Patent Nos. 4,772,530 and 4,772,541 are particularly preferred.

It is possible to use various compounds as the chromogenic materials in the present systems. If the

chromogenic material is encapsulated with the photosensitive composition, it should not interfere with the sensitivity of the system. One example of chromogenic material useful in practice of the invention is colourless electron donating compounds. Representative examples of such colour formers include substantially colourless compounds having in their partial skeleton a lactone, a lactam, a sulfone, a spiropyran, an ester or an amido structure such as triarylmethane compounds, bisphenylmethane compounds, xanthene compounds, fluorans, thiazine compounds, spiropyran compounds and tne like. Crystal Violet Lactone, Copikem X, IV and XI (products of Hilton-Davis Co.) and commercially available cyan, yellow and magenta colour forming agents may be used alone or in combination as colour precursors in our systems.

Photosensitive microcapsules useful in practice of the present invention are easily formed using conventional techniques such as coacervation, liquid-liquid phase separation, interfacial polymerization and the like. Various melting, dispersing and cooling methods may also be used.

The photosensitive compositions are usually oleophilic and can be encapsulated in hydrophilic wall-forming materials such as gelatin-type materials (see U.S. Patent Nos. 2,730,456 and 2,800,457 to Green et al.) including gum arabic, polyvinyl alcohol, carboxymethylcellulose; resorcinol-formaldehyde wall formers (see U.S. Patent No. 3,755,190 to Hart et al.); isocyanate wall-formers (see U.S. Patent No. 3,914,511 to Vassiliades); isocyanate-polyol wall-formers (see U.S. Patent No. 3,796,669 to Kiritani et al.); urea formaldehyde wall-formers, particularly urea-resorcinol-formaldehyde in which oleophilicity is enhanced by the addition of resorcinol (see U.S. Patent Nos. 4,001.140; 4,087,376 and 4,089,802 to Foris et al.); and melamine-formaldehyde resin and hydroxypropyl cellulose (see our U.S. Patent No. 4,025,455).

Our developer sheets are particularly useful in full colour imaging systems such as those described in U.S. Patent Nos. 4,772,530 and 4,772,541 the disclosures of which are to be regarded as incorporated herein by reference. The microcapsules used in full colour imaging individually contain cyan, magenta and yellow colour formers and photosensitive compositions having distinctly different sensitivities. A uniform mixture of the microcapsules is distributed over the surface of the imaging support. As is explained in more detail in the above-listed references, each set of microcapsules is primarily sensitive in a different wavelength band such that the microcapsules can be individually exposed with minimum cross-talk. In panchromatic systems, the cyan, magenta, and yellow forming photosensitive microcapsules are respectively sensitive to red, green and blue light.

In addition to being useful in photosensitive systems of the type described above, our developer sheets are also useful in conventional pressure-sensitive carbonless systems.

The present invention is illustrated in more detail by the following non-limiting examples:

Example 1

A 1-mil thick polyethylene terephthalate sheet was coated with three sets of photosensitive microcapsules respectively containing cyan, magenta and yellow colour forming agents and a photopolymerizable compound including a monomer and a photoinitiator to be used as a full colour-imaging sheet. As a control, the imaging sheet was aligned with a developer sheet comprising 5-mil polyethylene terephthalate having uniformly coated on its front surface a layer of Schnechtady HRJ-4252 particles coated at an amount of 8 g/m^2 so that the microcapsules contacted the developer particles. The assembly was then passed through a pair of pressure rollers at a pressure of 350 pli (6.13×10^4 N/m) to rupture the microcapsules and thereby enable the color-forming agents to migrate to the developer sheet. The imaging sheet was removed from the developer sheet and discarded, and the density of the image on the developer sheet was measured using a MacBeth densitometer. The measured density was .69.

Examples 2-13

The experiment of Example 1 was repeated with the exception that either: (a) the donor sheet had attached to its surface opposite to the surface contacting the microcapsules a backing sheet having different thicknesses prior to assembling the donor sheet with the developer sheet; or (b) the receiver sheet had attached to its surface opposite the surface containing the developer material a backing sheet having different thicknesses prior to assembling the donor sheet with the developer sheet. The backing material and measured density after transfer are set forth in Table 1.

Table 1

Paper Backing Experiment			
		(a)	(b)
Example	Backing Material	Donor Backed	Receiver Backed
1	Control	0.69	0.69
2	Luxe Kote (Mitsubishi Paper Mills)	0.78	0.75
3	Zanders 80 lb. Ironofix	0.75	0.74
4	Centura Dull (Consolidated)	0.78	0.76
5	80 lb. B and W Dull (Mead)	0.75	0.74
6	White A New Paramount (Oji)	0.72	0.74
7	Lustro Dull (S.D. Warren)	0.72	0.73
8	Pearl Kote (Mitsubishi Paper Mills)	0.77	0.72
9	Centura Dull Text (Consolidated)	0.73	0.72
10	Moistrite (Mead)	0.78	0.82
11	Mead Matrix	0.74	0.75
12	Vintage Velvet 80 lb. Dull (Potlash)	0.73	0.73
13	Mead Cocklebond	0.73	0.76

In every instance, the use of a backing sheet on either the donor or developer sheet produced higher density images.

Example 14

As a control developer sheet 5 mil polyethylene terephthalate was coated with a uniform layer of HRJ-4542 particles at an amount of 8 g/m^2. The thickness of the layer was approximately 8 microns. For use as a donor sheet 1 mil polyethylene terephthalate was coated with a set of full color photosensitive microcapsules containing cyan, magenta and yellow color-forming agents. The donor and developer sheets were aligned so that the microcapsules contacted the developer material, the assembly was passed through a pair of pressure rollers operating at 350 pli (6.13 x 10^4 N/m) and the donor sheet was detached and discarded from the developer sheet. The density of the produced image for each of the colors, as well as the percent haze for the samples is set forth in Table 2.

Examples 15-16

The experiment of Example 14 was repeated with the exception that a stilt material was added to the developer particles prior to coating the developer material onto the developer substrate. For a stilt material, photohardened microcapsules were utilized. Prior to photohardening, the microcapsules contained in their internal phase 150 parts photohardenable monomer (TMPTA), 0.4 parts photoinitiator, 1,1-di-n-heptyl-3,3,3′,3′-tetramethyl indocarbocyanine triphenyl-n-butyl borate, 36 parts magenta color forming agent (Hilton Davis HD-5100) and 1.5 parts 2,6-diisopropyl dimethylaniline. The microcapsules were placed in a one-liter round bottom flask and exposed to light from a 15-watt cool-white fluorescent tube for 24 hours to fully polymerize the TMPTA and harden the microcapsules. The diameter of the hardened microcapsules ranged from about 3 microns to about 10 microns. A developer coating layer was produced by mixing 99.9% of the developer material of Example 14 and 0.1% of the hardened microcapsules (W/W). The experiment of Example 14 was repeated and the results are set forth in Table 2. Similarly, a coating layer was produced by mixing together 99.5% of the developer material of Example 14 and 0.5% of the hardened micro-capsules (W/W). The results are set forth in Table 2.

Table 2

Example	Sample	Cyan density	Magenta density	Yellow density	Black density	Haze
14	control	0.45	0.26	0.41	0.61	11.6
15	0.1% stilt material	0.50	0.29	0.42	0.67	12.7
16	0.5% stilt material	0.48	0.29	0.44	0.68	12.0

As seen by the data, the addition of the stilt material increased the density of the image produced from each of the colour-forming reactions.

Claims

1. A developer sheet useful in forming images having a high density, said sheet comprising a support having front and back surfaces wherein said support is microroughened to provide a discontinuous texture; and a developer layer containing a particulate reactive material on said front surface, said reactive material being capable of reacting with a substantially colourless chromogenic material upon contact and generating an image.

2. A developer sheet useful in forming images having a high density, said sheet comprising a support having front and back surfaces and a developer layer consisting essentially of a particulate reactive material and a stilt material on said front surface, said reactive material being capable of reacting with a substantially colourless chromogenic material upon contact and generating an image, and said stilt material being capable of absorbing a high pressure load to prevent said reactive material from substantially deforming upon the application of a high pressure load.

3. A developer sheet useful in forming images having a high density, said sheet comprising: a support having front and back surfaces; a backing layer having front and back surfaces; and a developer layer containing a particulate reactive material; said front surface of said backing layer being attached to said back surface of said support, said backing layer being texturally discontinuous, said developer layer being located on said front surface of said support, and said reactive material being capable of reacting with a substantially colourless chromogenic material upon contact and generating an image.

4. A developer sheet according to any preceding claim, further characterised in that said sheet is adapted for use in a photosensitive imaging system.

5. A developer sheet according to Claim 4, further characterised in that said reactive material comprises an electron accepting compound.

6. A developer sheet according to Claim 5, further characterised in that said electron accepting compound is selected from acid clays, aromatic carboxylic acids and polyvalent metal salts thereof, phenolic resins and polyvalent metal salts thereof, and polymers of aromatic carboxylic acids with aldehydes or acetylene and polyvalent metal salts thereof.

7. A developer sheet according to any preceding claim, further characterised in that said support comprises a polymeric material, preferably polyethylene terephthalate.

8. A developer sheet according to any of Claims 1 to 6, further characterised in that said support comprises polymer coated paper.

9. A developer sheet according to Claim 1 or any claim appendant thereto, further characterised in that said microroughened support comprises a substrate having alternating regions of relatively high and relatively low substrate thickness, and in that the space separating said alternating regions ranges from between about 10 microns and about 40 microns.

10. A developer sheet according both to Claim 1 and either of Claims 7 or 8, further characterised in that a pigment is optionally included in the polymer substrate or coating prior to formation of said support into a sheet; and in that said support is microroughened by the steps of either calendaring the polymeric support or polymer coating against a roughened roller after said sheet formation, or solvent etching the polymeric support or polymer coating after said sheet formation, or casting the polymeric substrate or coating against a rough surface prior to said sheet formation.

11. A developer sheet according to any of Claims 1 to 8, further characterised in that said sheet further comprises a discontinuous layer of a thermoplastic polymeric pigment overlying said developer layer, said polymeric pigment being capable of forming an essentially transparent film upon the application of heat or

pressure.

12. A developer sheet according to Claim 2 or any claim appendant thereto, further characterised in that said stilt material is selected from starch particles, pulp materials, polyolefin materials and hardened spherical particles.

13. A developer sheet according to Claims 2 or 12, further characterised in that the diameter of said stilt material ranges from about 6 microns to about 20 microns.

14. A developer sheet according to Claim 3 or any claim appendant thereto, further characterised in that said backing layer is either adhered to said support or is integrally formed on said support.

15. A developer sheet according to Claim 3 or Claim 14, further characterised in that said backing layer comprises a material having alternating regions of relatively high and relatively low thickness, and in that the space separating said alternating regions ranges between about 10 microns and about 40 microns.

16. Imaging means comprising an imaging sheet including a support having a layer of photosensitive microcapsules on the surface thereof, said microcapsules containing a photohardenable or photosoftenable composition as the internal phase and having a chromogenic material associated therewith; and a developer sheet, characterised in that said developer sheet comprises a developer sheet according to Claim 4 or any claim appendant thereto, said chromogenic material and said developer material being selected to be capable of reacting to form a visible image on said developer sheet.

17. Imaging means according to Claim 16, further characterised in being adapted to produce full colour visible images.

18. Imaging means, comprising: a donor sheet comprising a support having front and back surfaces, a backing layer having front and back surfaces, and a receiver sheet having front and back surfaces; the donor sheet having a layer of microcapsules containing in their internal phases a substantially colourless chromogenic material coated on its front surface, the front surface of said backing layer being attached to the back surface of said donor sheet, and said backing layer being discontinuous in thickness; and said receiver sheet containing a developer material containing a particulate reactive material on its front surface, said reactive material being selected to be capable of reacting with said substantially colourless chromogenic material upon contact and to generate an image..

19. Imaging means according to Claim 18, further characterised in that said imaging means is adapted for use in a photosensitive imaging system, said internal phase of said microcapsules additionally containing a photohardenable composition.

20. Imaging means according to Claims 18 or 19, further characterised in that said backing layer is either adhered to said donor sheet or is integrally formed on said sheet.

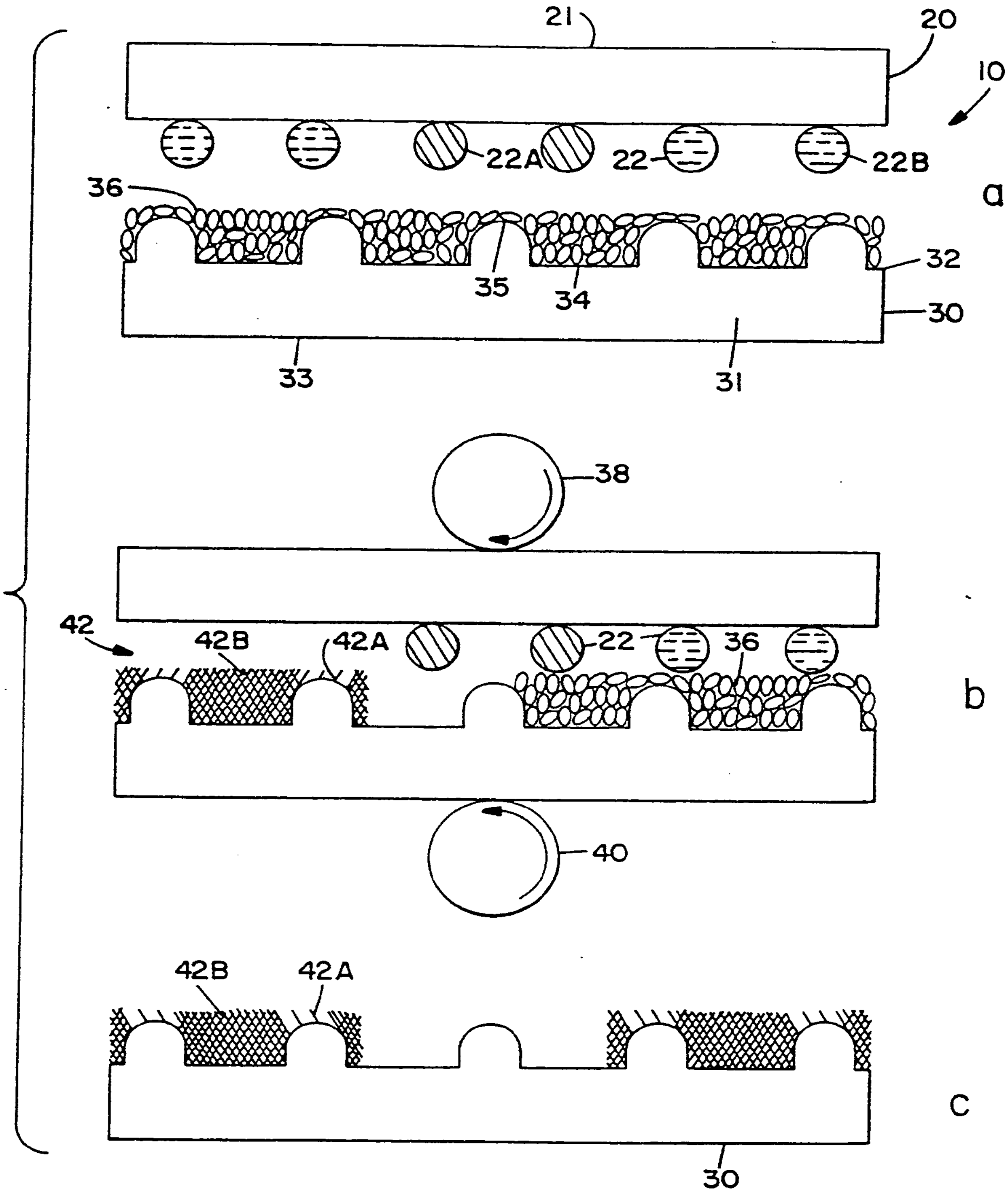
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FIG. I

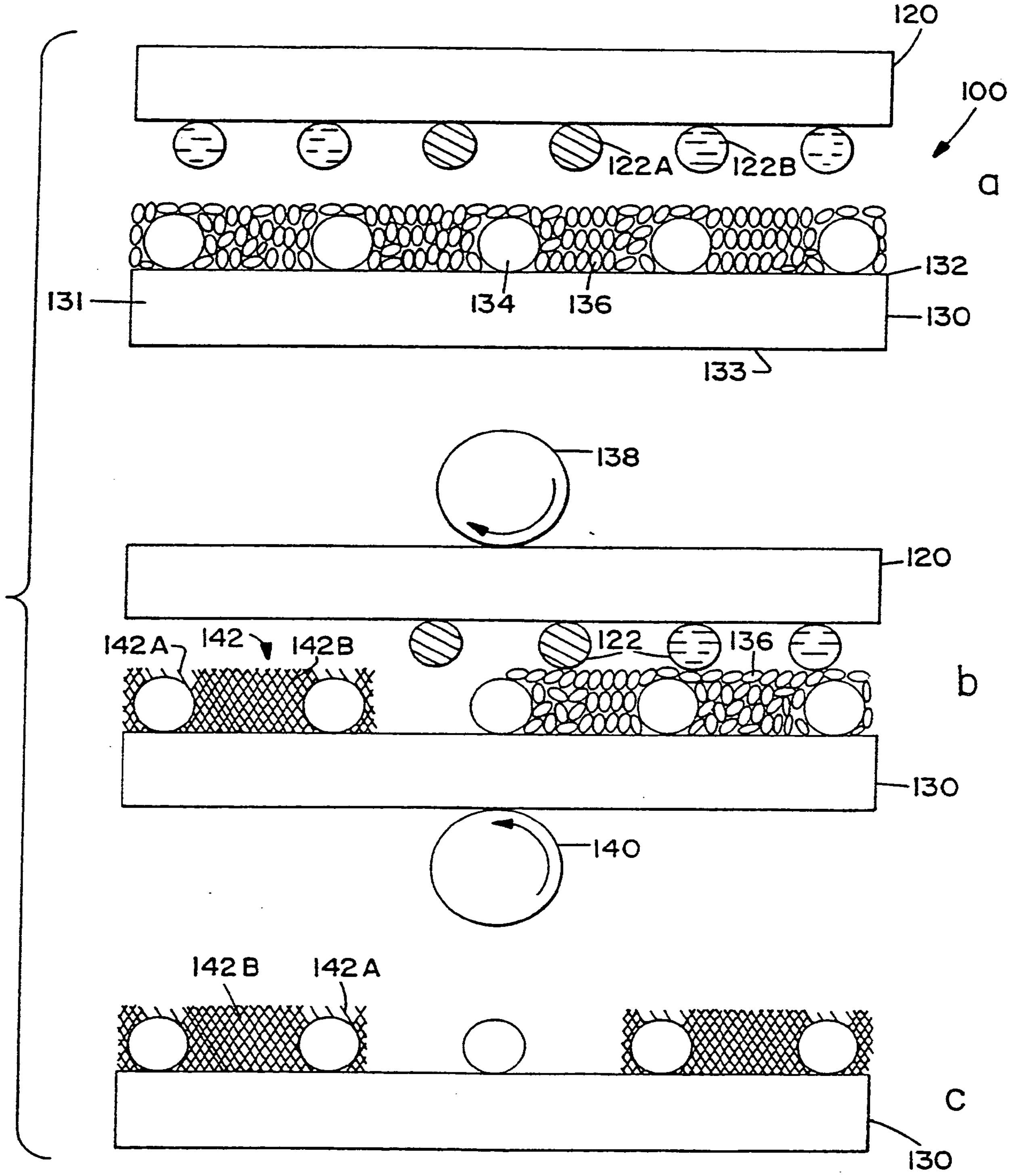
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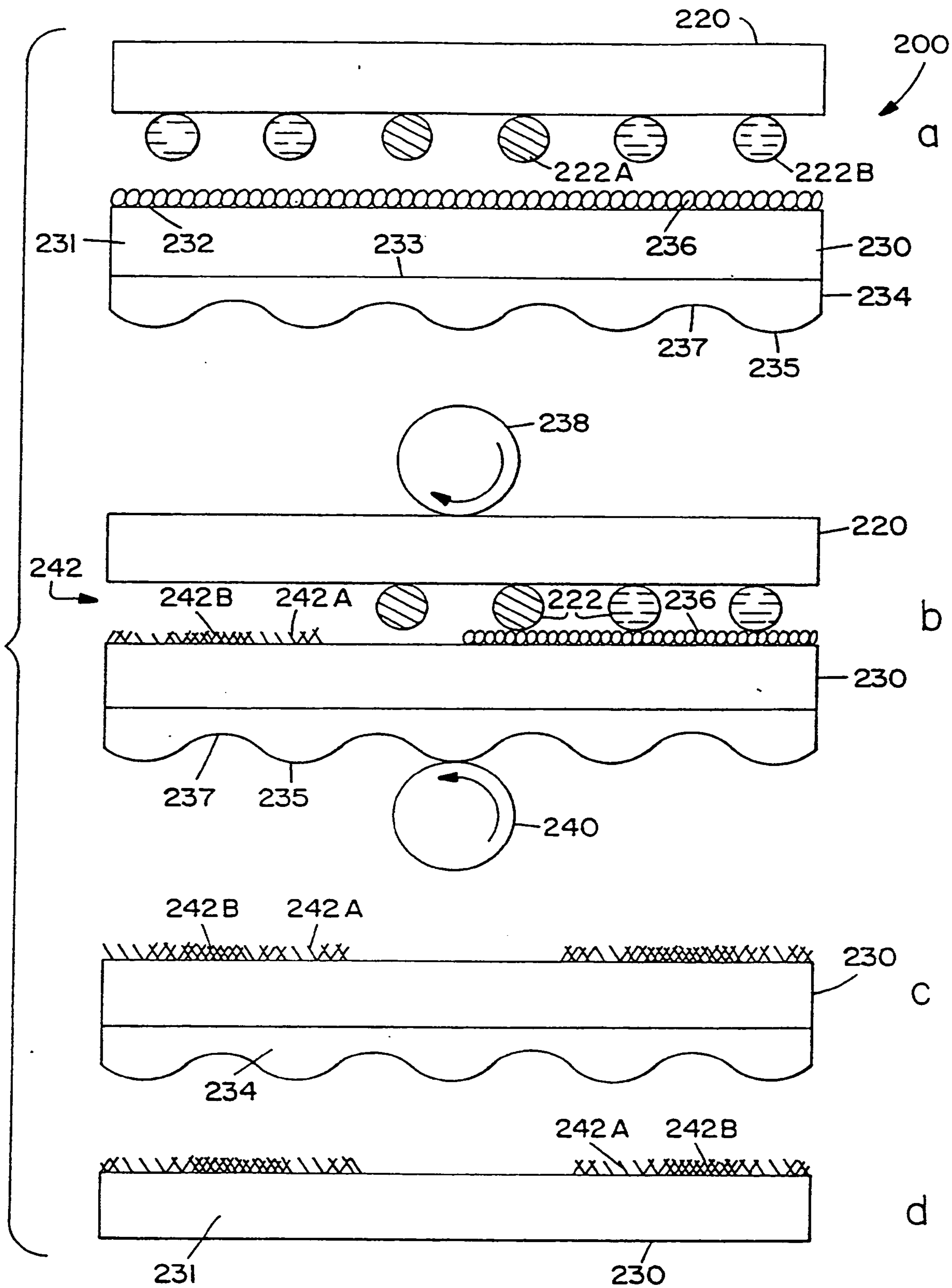
FIG. 2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242A
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242A
242B
d
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230

FIG. 3

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(54) Developer sheet and imaging means, both for forming images.

(57) Developer sheets for producing high density images, preferably in a photosensitive imaging system are disclosed. The developer sheet contains a particulate developer material which does not substantially compress upon the application of pressure to the sheet. The resistance to pressure is accomplished by using a developer sheet which has a discontinuous thickness or by incorporating a stilt material into the developer material. Also disclosed is imaging means which has a discontinuous thickness donor sheet to prevent the developer material from substantially compressing upon the application of pressure.

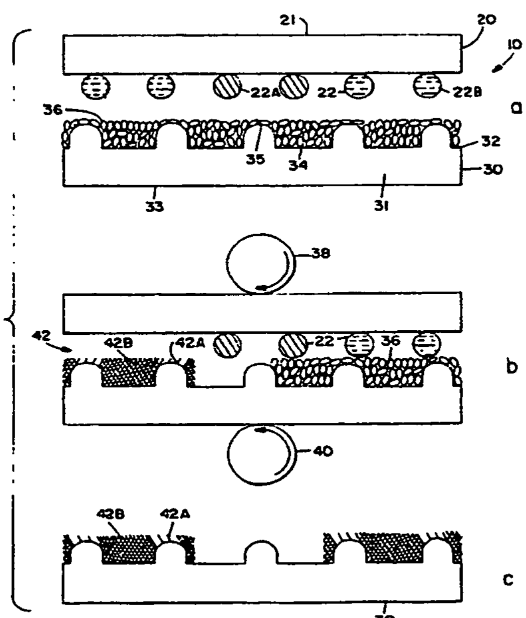

FIG. I

EP 0 372 927 A3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 31 2712

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X,Y	US-A-4089547 (C. BRYNKO ET AL.) * column 2, line 59 - column 3, line 2 *	1-20	B41M5/155 G03F7/00
Y	PATENT ABSTRACTS OF JAPAN vol. 6, no. 45 (M-118)(923) 20 March 1982, & JP-A-56 161197 (MITSUBISHI SEISHI K.K.) 11 December 1981, * the whole document *	1-20	
A	US-A-4223060 (P.R. RAINE ET AL.) * the whole document *	1-20	
A	EP-A-76342 (MITSUBISHI PAPER MILLS LIMITED) * the whole document *	1-20	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B41M G03F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	08 MAY 1990	BACON A.J.

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CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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